BERKELEY LAB

High Energy Density Electrodes *via* Modifications to the Inactive Components and Processing Conditions

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LBNL

June 9, 2017

Project ID #
ES232

Overview

Timeline

- Project start date: 10/1/2016
- Project end date: 9/31/2018
- Percent complete: 50%

Budget

- Total project funding
  - DOE share: 100%
  - Contractor share: 0%
- Funding received in FY 2016
  - $1 M
- Funding for FY 2017:
  - $1 M (2.5 FTEs)

Barriers

- Barriers addressed (EV)
  - A. *Cost* - $133/kWh
  - C. *Performance* - 2/1 P/E for 30 seconds at 80% DOD
  - E. *Life* - 10 years

Partners

- Interactions / collaborations
  - Arkema
  - Umicore
  - Black Diamond Structures
  - Daikin America
  - Applied Spectra
  - BMR Program and LBNL
    - D. Wheeler (BYU)
    - S. Harris (LBNL)
    - D. Parkinsen (LBNL)
    - G. Liu (LBNL)
    - K. Zaghib (HQ)

Relevance: Objectives and Impact

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- Project Objective:

  To establish fundamental engineering principles in the fabrication of electrode laminates based on material and rheological properties.

  - Work this year (from Apr. ’16 to Mar. ’17):
    - Investigated the effect of calendering
    - Investigated the fraction of inactive components in the laminate
    - Investigated the application of carbon nanotubes
    - Investigated the impacts on cycle life

- Relevance to VT Office:

The VT Office is bolstering the penetration of electric vehicles by supporting research into the barriers preventing their adoption. Two of the main barriers are cost per kWh and energy density. This research addresses both.

- Impact:

If successful, this effort will result in an increase in the cathode’s potential energy density by as much as 25 % which will increase range and reduce cost per kWh. This will have a significant impact on the market acceptance of EVs.

Issues of Thick Electrodes

General Questions

- Is the implementation of thick electrodes limited by manufacturing capability or performance?
  - If using the standard formulation – limited by processing conditions

    Thick electrodes –
    - Show cracks
    - Easily delaminate
    - Show segregation of carbon and active material
- Can we develop sound, fundamental principles to help OEMS select materials to engineer their way around this problem?

Milestones

Date	Milestones and Go/No-go Decisions	Status
December 2015	Fabricate laminates of NCM cast to different thicknesses using standard materials and various processing conditions to determine their effect on overall electrode quality.	Met
March 2016	Fabricate laminates of NCM cast to different thicknesses using higher molecular weight binders and various processing conditions to determine their effect on overall electrode quality.	Met
June 2016	Fabricate laminates of NCM cast to different thicknesses using standard materials and various processing conditions on current collectors with a thin layer of binder and conductive additive pre-coated on the current collector to determine their effect on overall electrode quality.	On going
September 2016	Go/No-go. Determine if a high molecular-weight binder or pre-coated current collector is worth pursuing to achieve thicker electrodes based on ease of processing and level of performance.	On going

Milestones

Date	Milestones and Go/No-go Decisions	Status
December 2016	Fabricate “thick” laminates of NCM and establish the effect of calendering at different temperatures.	Met
March 2017	Investigate the use of carbon additives in the form of carbon nanotubes.	On going
June 2017	Determine the degree to which several updates in materials and processing are affecting cycleability.	On schedule
September 2017	**Go/No-go**. Determine if a binder of a mixture of molecular weights is worth pursuing to achieve thicker electrodes based on ease of processing and level of performance. If no, pursue a path of a single molecular weight binder.	On schedule

Technical Approach/Strategy

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To investigate a number of modifications to materials and process conditions toward the fabrication of ultra-high loading electrodes, utilizing a suite of diagnostic tools including those that address the relationship of stress and strain from the slurry to the final laminate and to use those relationships to develop engineering principles in the fabrication of battery electrodes.

Materials | *Process Conditions* | *Diagnostics* | *Engineering Principles*

umicore

ARKEMA

BYU

BERKELEY LAB

APPLIED SPECTRA

2015 → **2016** → **2017** → **2018**

Effect of material properties and processing conditions on electrode uniformity

Combinations of materials and processes that provide engineering principles to electrode manufacturing.

Combination of materials and processes that can be performed today

BLACK DIAMOND STRUCTURES

DAIKIN

Hydro Québec

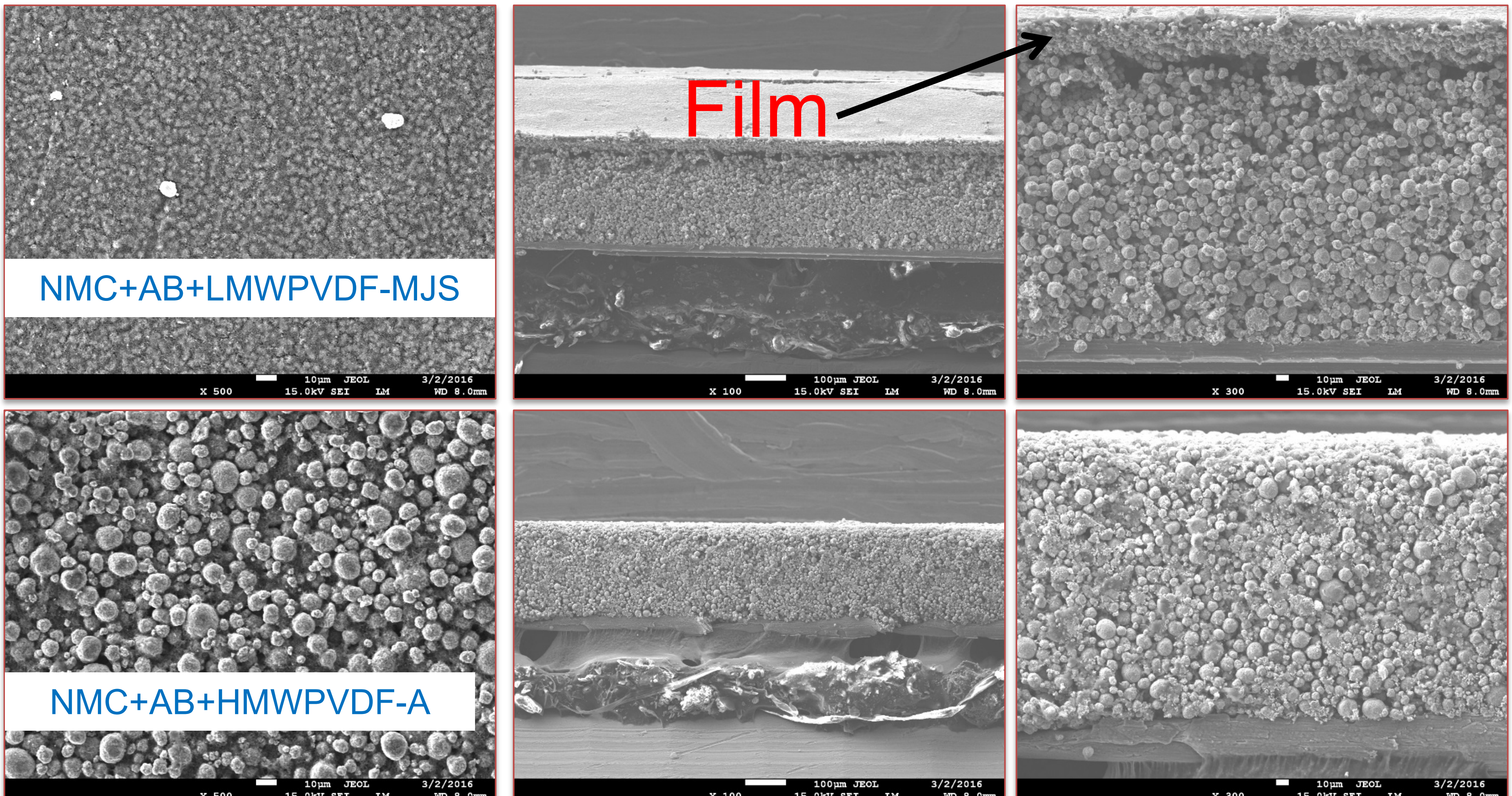
ALS Synchrotron Infrared Beamlines

Hydro Québec

Technical Accomplishments

Previous Year

Surface | Cross section | Cross section



A higher molecular-weight binder results in a more uniform electrode.

Technical Accomplishments

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Previous Year

From October '15 to March '16:

1. Assessed binders from two vendors on
    1. Solubility in NMP
    2. Ability to make comparable electrodes.
    3. Electrode uniformity
2. Assessed electrode processing conditions
    1. Slurry viscosity
    2. Casting speed
    3. Height of doctor blade
3. Assessed electrode performance (power and energy)
    - Electrode thickness
    - Electrode porosity

Technical Accomplishments

This Year

Since March of 2016:

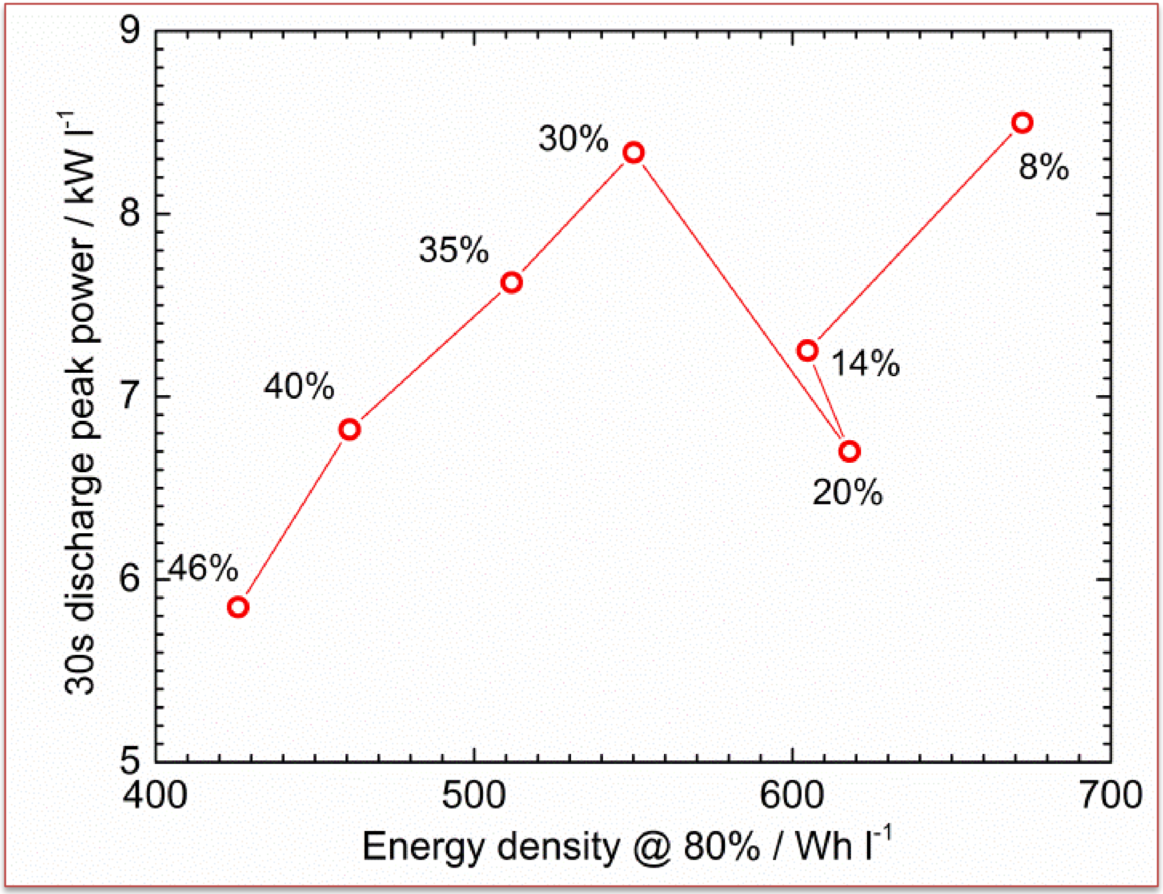
1. Assessed the effects of calendering
   - To different porosities
   - At different temperatures
   - On maintaining thickness

2. Mechanical Properties
   - Assessed polymer fraction
   - Assessed the effect of carbon nanotubes

3. Preliminary Cell Testing (Half- Coin-cells)
   - Rate capability
   - Power capability
   - Cycle life

Tech Acc. #1: Calendering

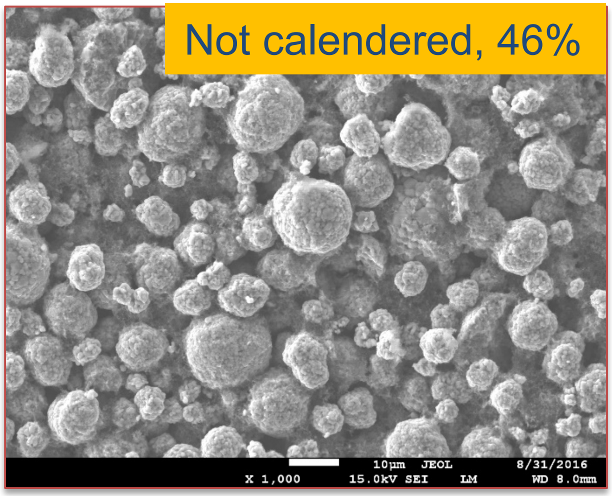
Standard electrode formulation calendered to different porosities at 100°C

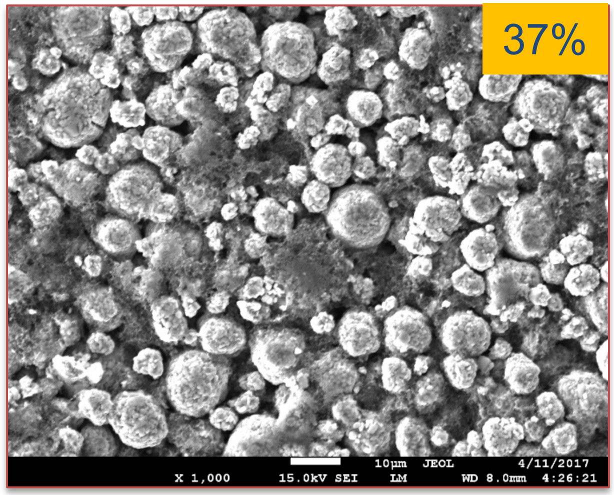


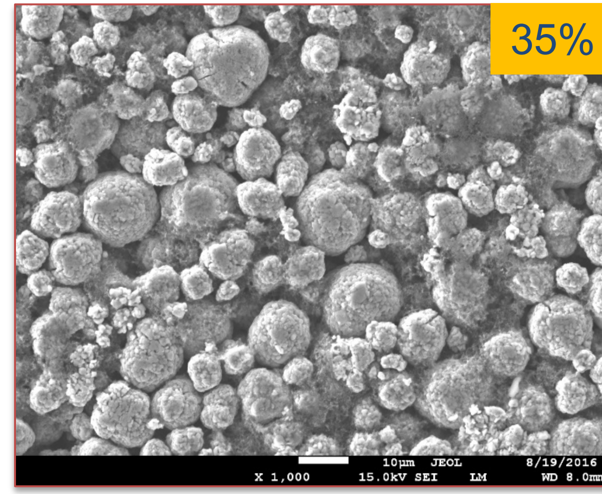
Electrodes calendered below 30% porosity demonstrate erratic power capability.

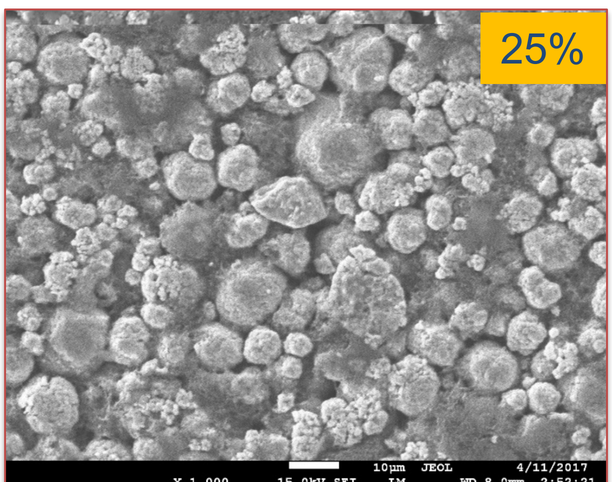
Tech Acc. #1: Calendering

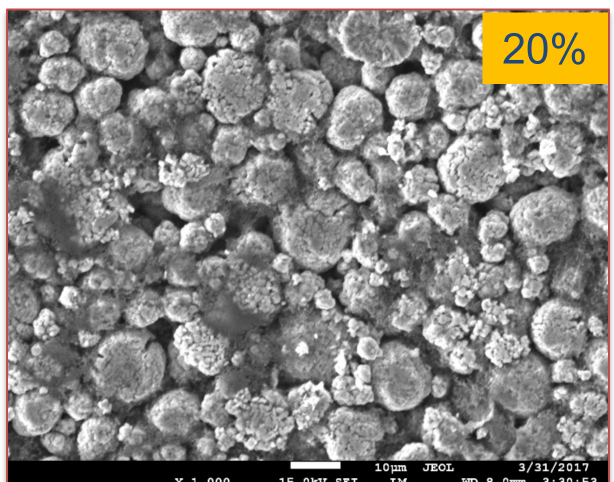
SEM Images of Electrode Surfaces (1000x)







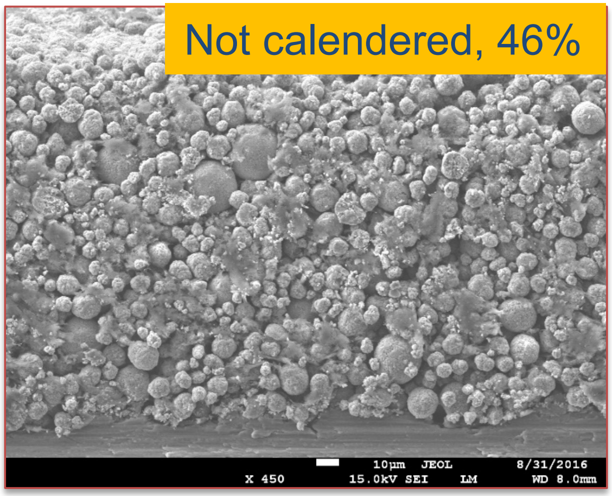


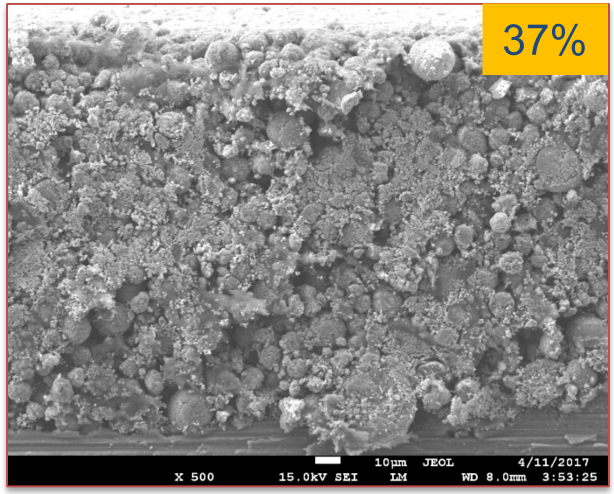


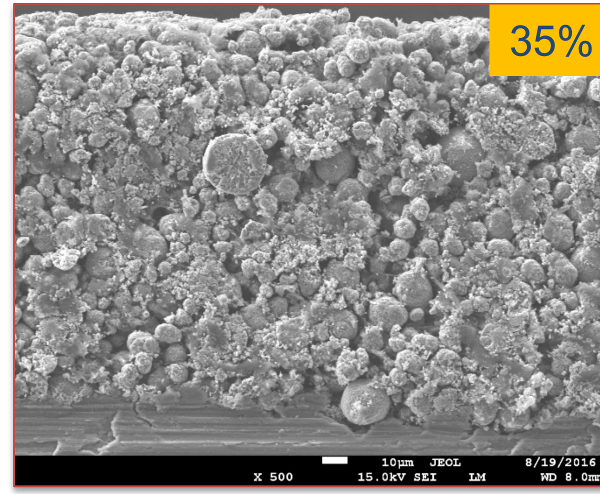
All calendered electrodes show at least some flattened secondary particles on the surface.

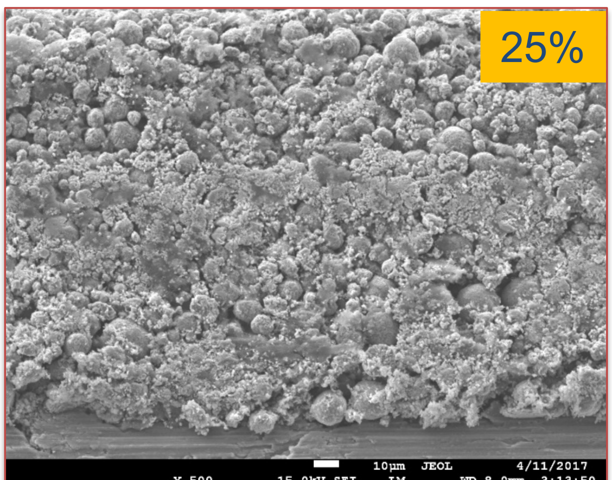
Tech Acc. #1: Calendering

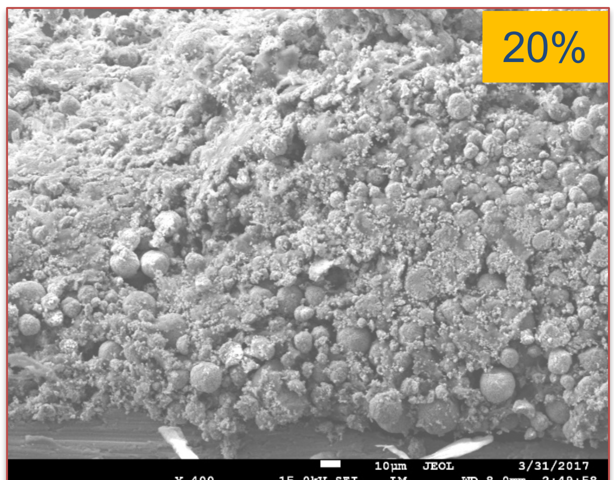
SEM Images of Electrode Cross-sections (1000x)









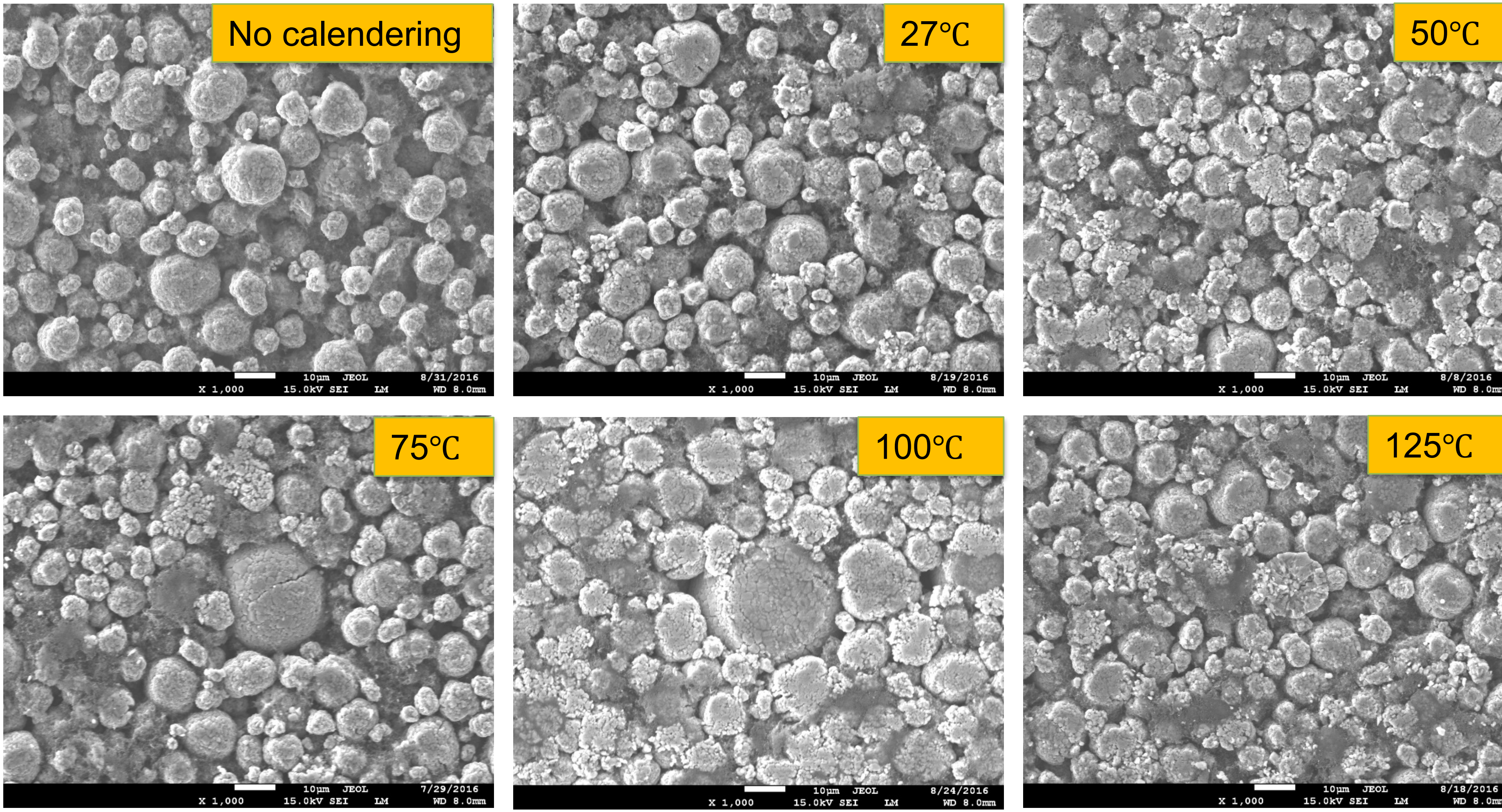


All calendered electrodes show that the secondary particles are more suscep-tible to break-up during cross-sectioning.

Other data indicates that the break-up only occurs at the cross-sectioned plain.

Tech Acc. #1: Calendering

SEM Images (Surface; 1000 x)



electrodes are calendered to 110 microns, 30% porosity

Flattened surfaces occur, independent of calendering temperature.

Tech Acc. #1: Calendering

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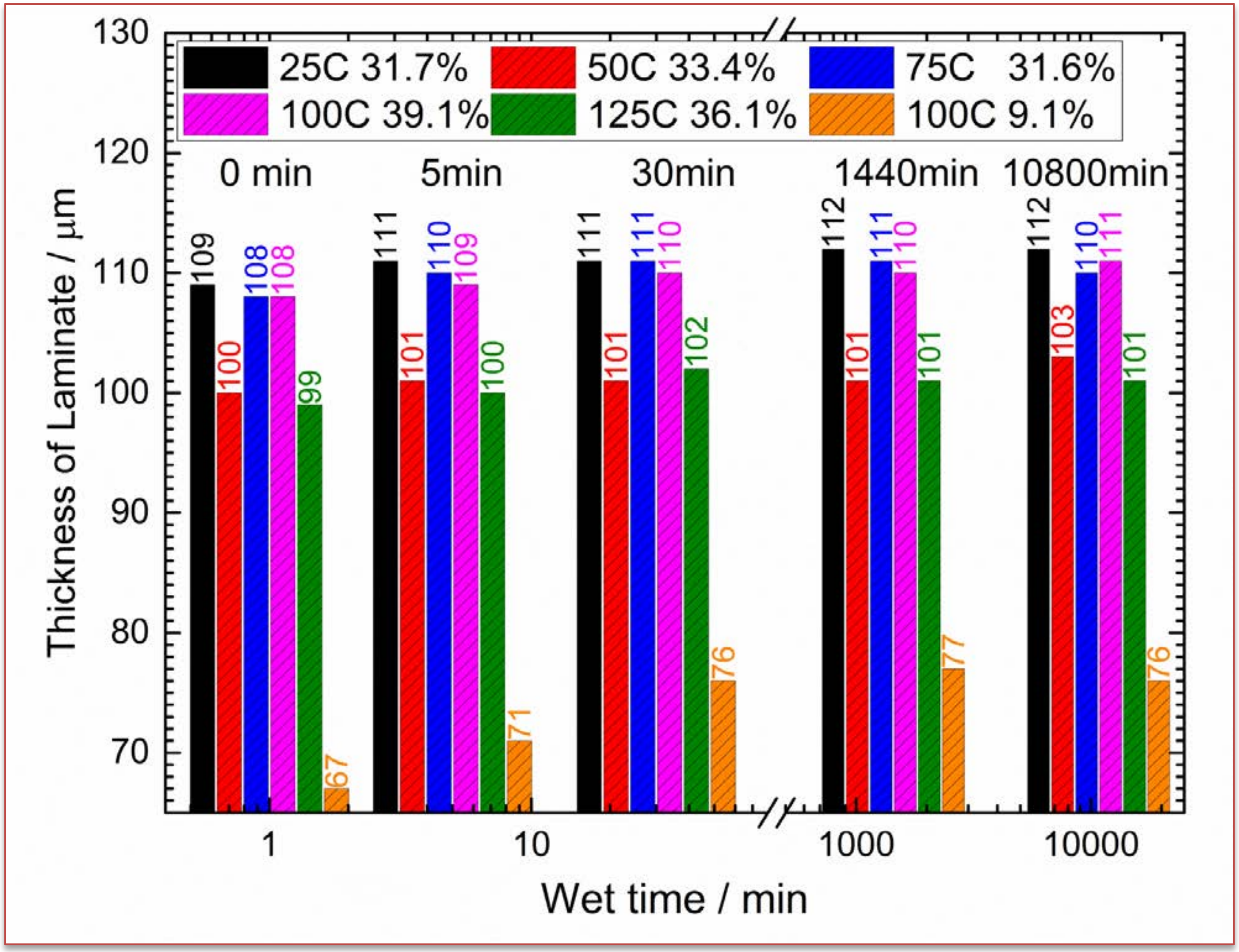
Laminate Thickness Changes with Soaking in Electrolyte

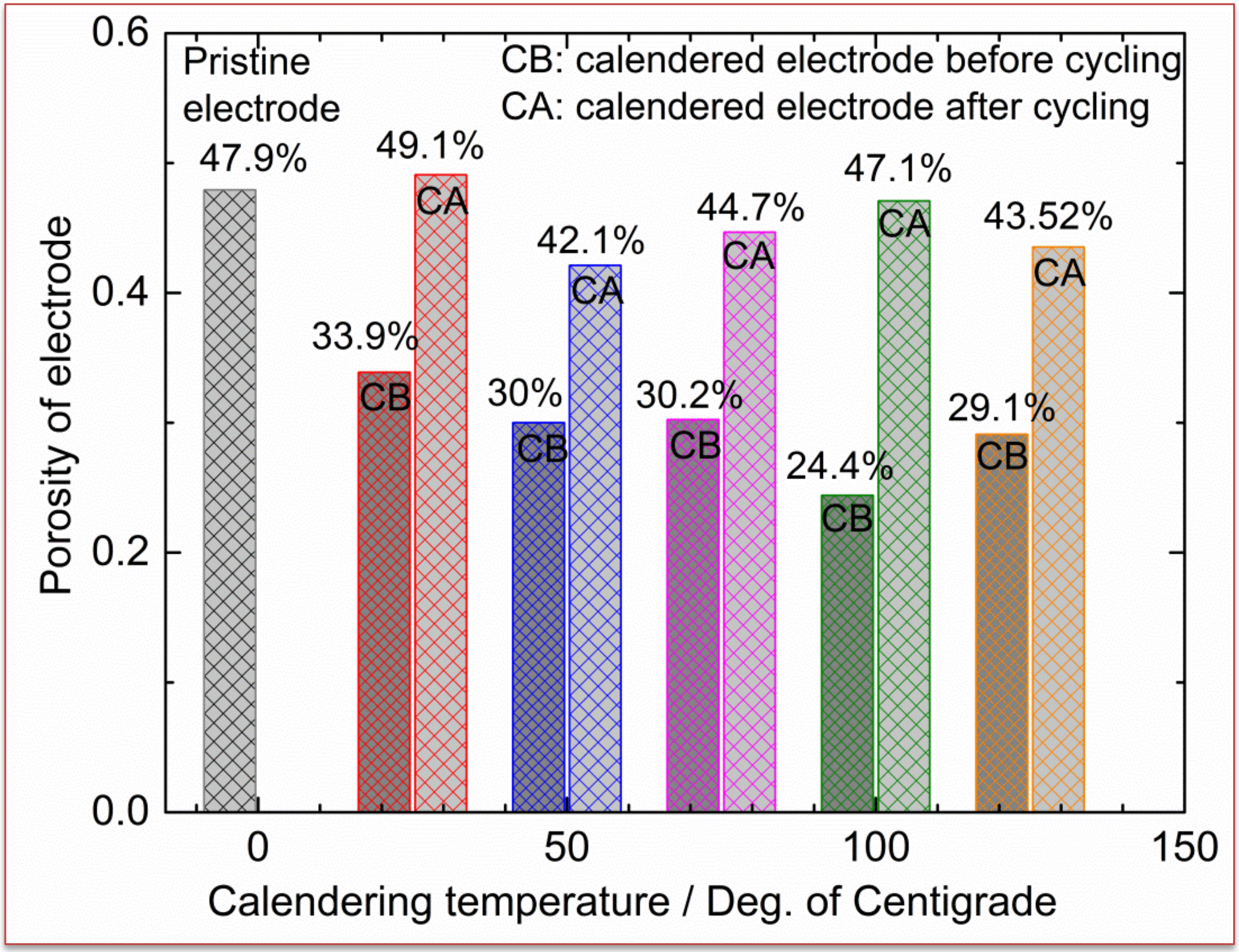
Calendered at Different Temperatures



Unless calendered to very low porosities,
no change in thickness with time (7.5 days).

Tech Acc. #1: Calendering

Calendered Laminate Thickness After Cycling



Electrodes cycled in coin cells recover most of their pre-calendered thickness by the 500th cycle.

Tech. Acc. #2: Mechanical Properties

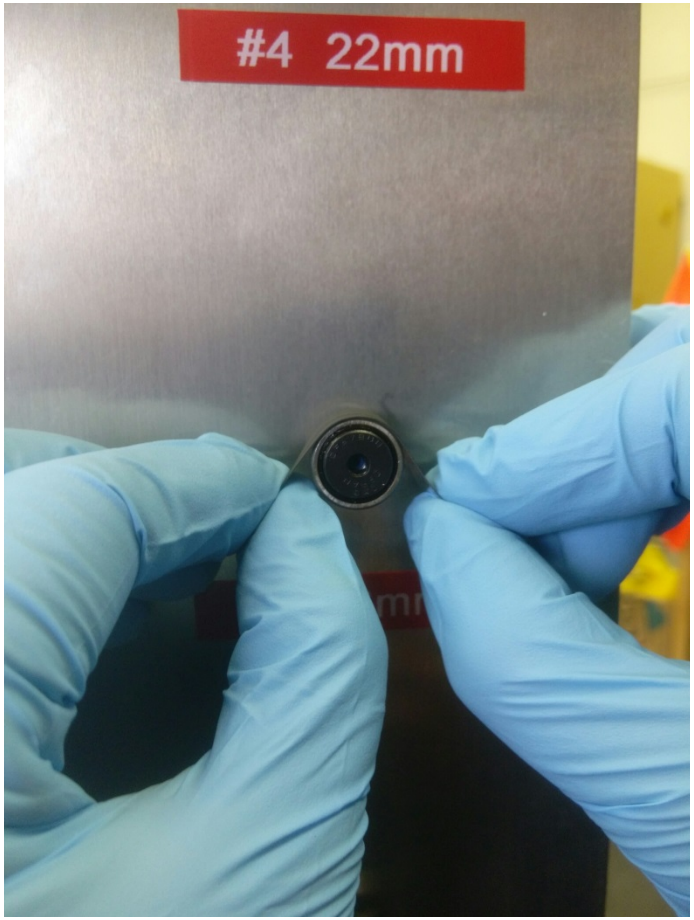
The flexibility of a polymer composite will largely depend on the properties of the polymer.

- PVDF is considered to be a fairly stiff polymer.
- Optimization
  - Low polymer fraction stretches the polymer too thin to withstand cracking
  - High polymer fraction makes the laminate too stiff.
  - A bend test can help assess the adhesivity and cohesivity of a laminate.

Investigated the fraction of polymer in the laminate.

Tech. Acc. #2: Mech. Properties

Procedures
1. Electrodes are cast and calendered to 40% porosity
2. 1 cm wide strips are cut from laminate
3. Laminate wrapped around spindles of ever decreasing diameter.
4. Fissures sought with SEM at 50x magnification.



Tech. Acc. #2: Mech. Properties

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Electrodes of Different Thicknesses and Binder Content Evaluated
Carbon Additive-to-Binder Ratio Held Constant

Sample formulation NMC/AB/PVDF wt	Laminate Thickness (µm)	Minimum roller number	Minimum roller diameter (mm)
98.2/0.8/1	240	#1	32
98.2/0.8/1	160	#12	4.8
96.4/1.6/2	280	#5	19
96.4/1.6/2	245	#5	19
96.4/1.6/2	125	#12	4.8
94.6/2.4/3	280	#5	19
94.6/2.4/3	260	#6	16
94.6/2.4/3	192	#12	4.8
92.8/3.2/4	310	#4	22
92.8/3.2/4	250	#6	16

(*all electrodes calendered to 40% porosity*)

Tech. Acc. #2: Mech. Properties

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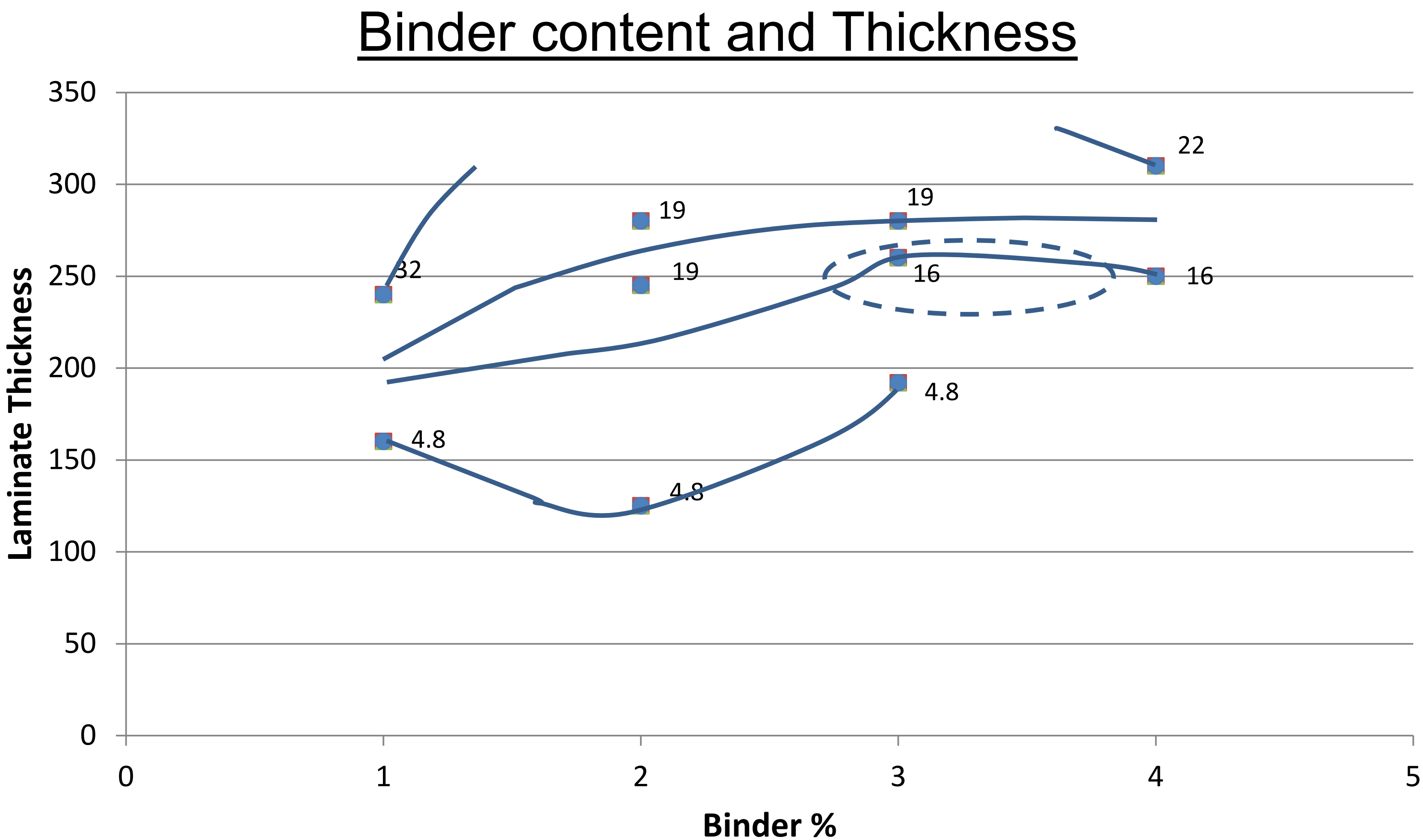
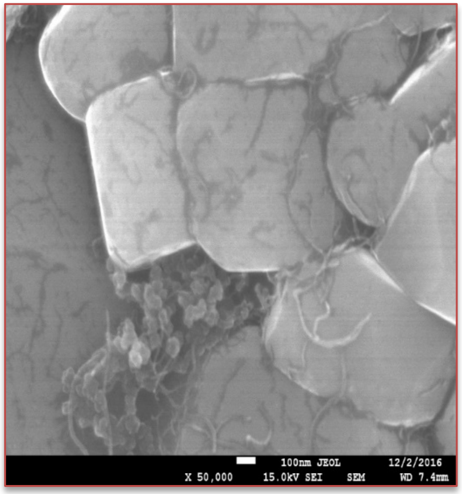


An electrode made of a high-molecular-weight binder, content of *ca*. 3 to 4 %, is sufficient for electrodes of around 250 microns.

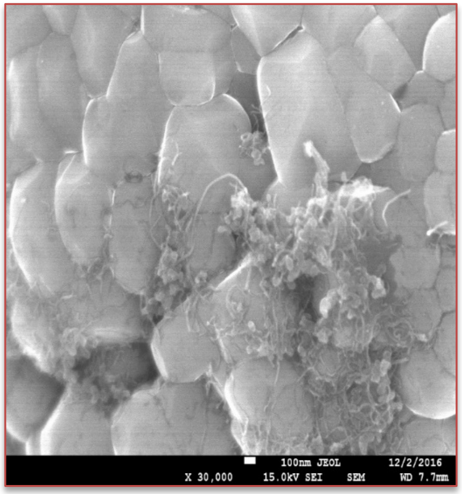
Tech. Acc. #2: Mechanical Properties

SEM Images of Electrode Incorporated with CNT (0.2 wt %)

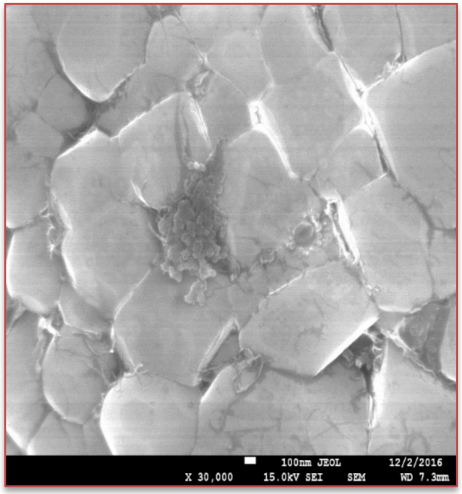
Bottom



Cross section



Surface

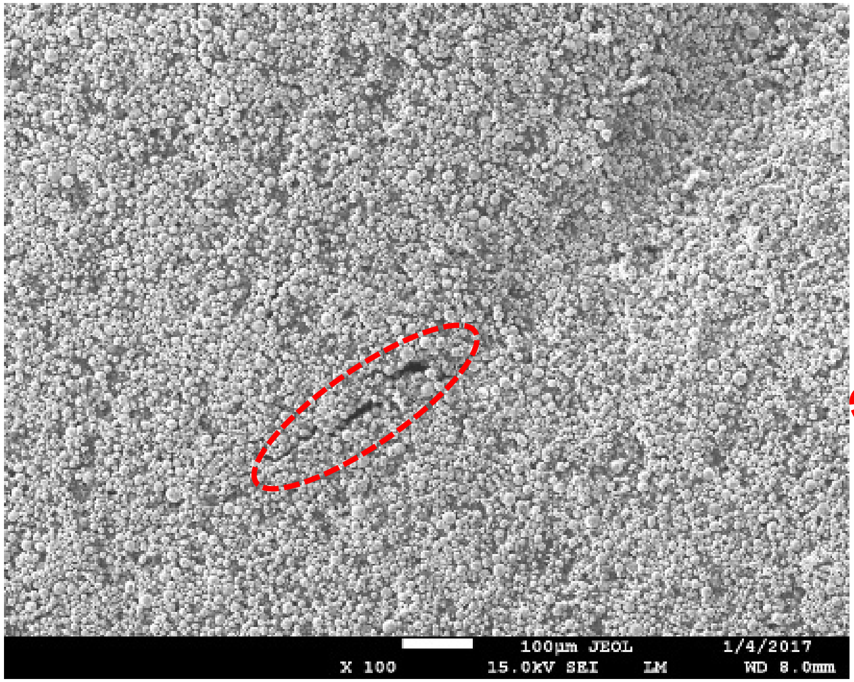


Nanotubes dispersed throughout electrode.

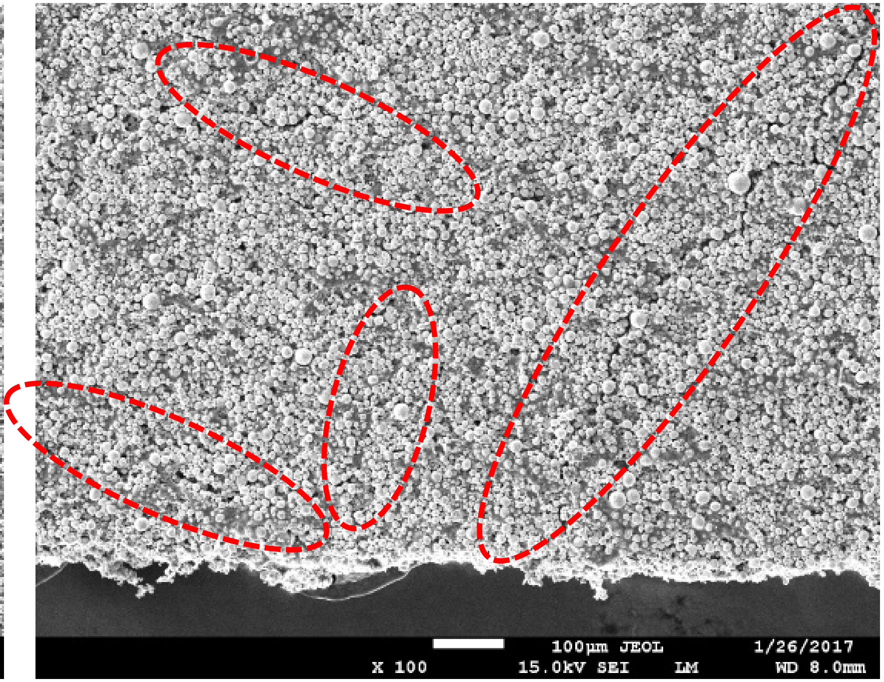
Tech. Acc. #2: Mech. Properties

Bend Test (32 mm dia.)

251 mm, 40% porosity, w/ 0.2% CNTs



212 mm, 40% porosity, w/o CNTs



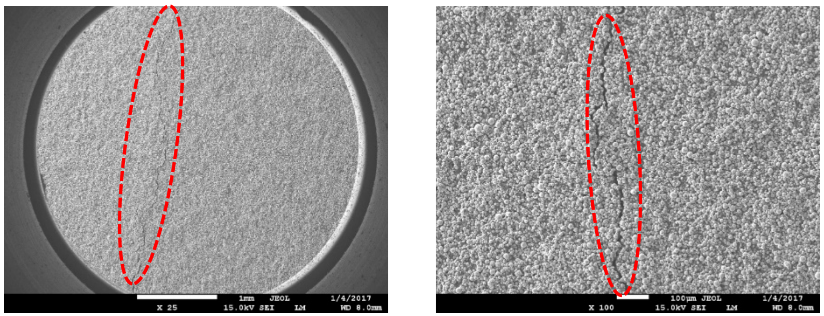
A small amount of CNTs appears to reduce fracturing.

Tech. Acc. #2: Mech. Properties

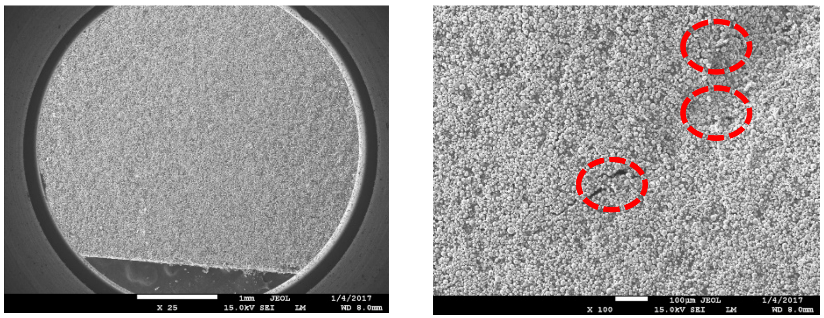
Bend Test of Electrodes of Varying Thicknesses

<u>32 mm dia. roller</u>

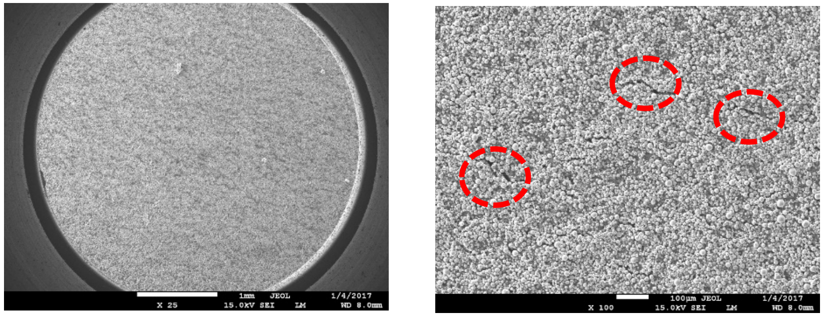
270 μm



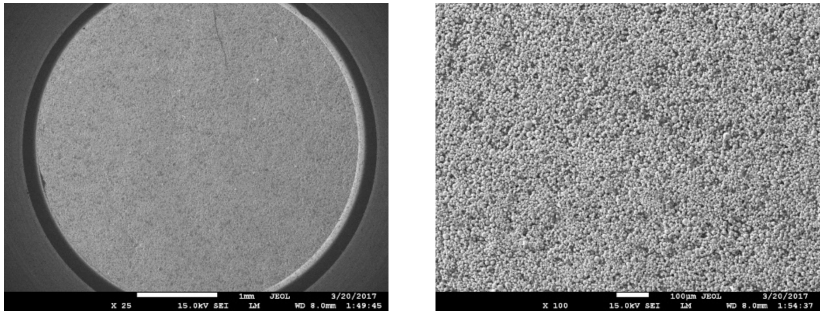
251 μm



232 μm



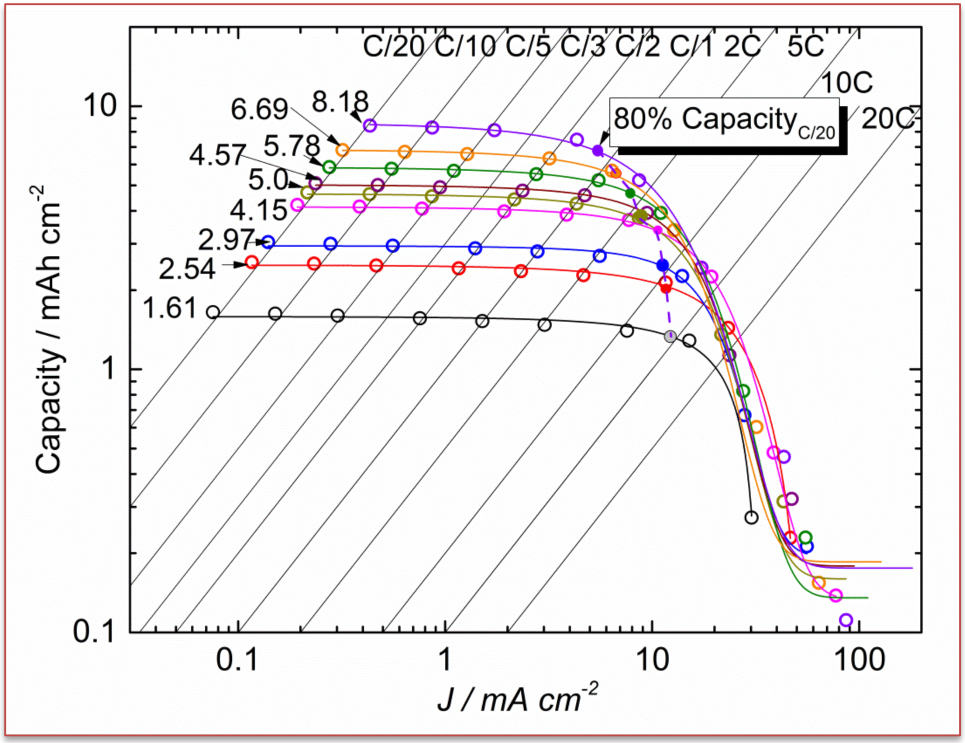
212 μm



Calendering reduces the likelihood of fracture from a bend test.

Tech. Acc. #3: Prelim. Cell Testing

<u>Discharge Performance of Electrodes of Various Loadings</u>

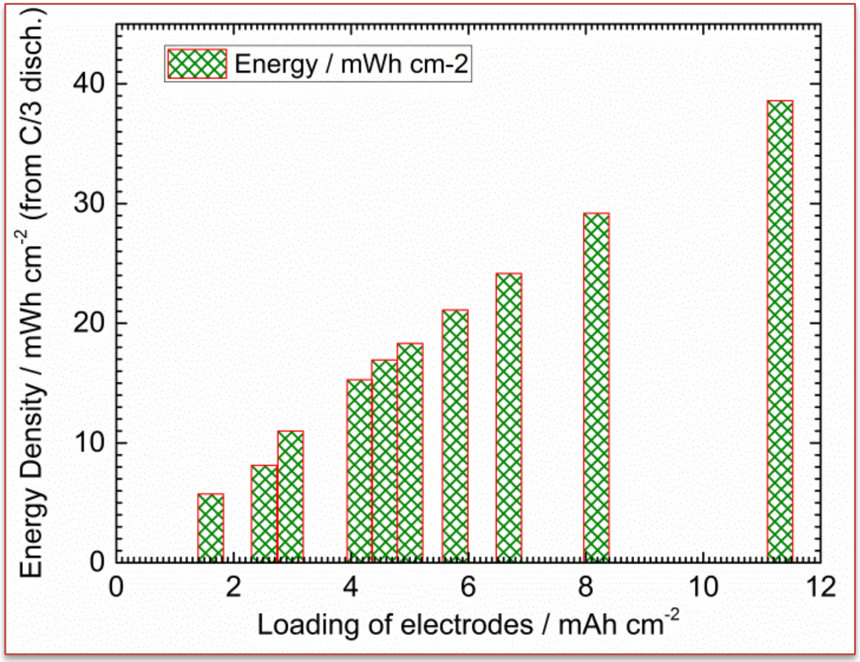


(40% porosity)

Electrodes of high loadings (>6.7 mAh/cm²) are capable of C/3 discharge.

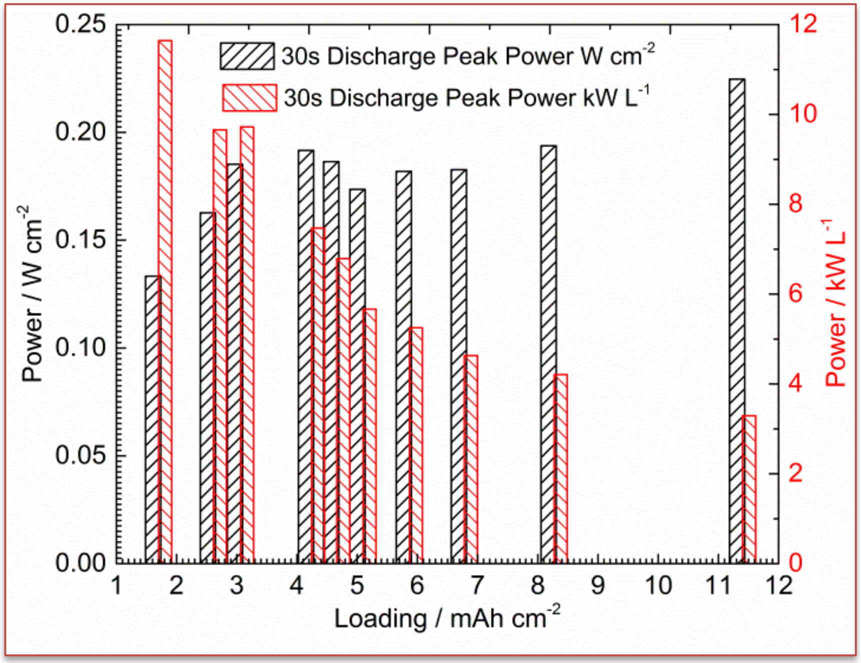
Tech. Acc. #3: Prelim. Cell Testing

Area Specific Energy (C/3)



(40% porosity)

Area Specific Pulse Power (30 s)



Power to Energy Ratio at 8 mAh/cm^2 = 190/(29x0.8) h^{-1} = 8.2 h^{-1}

Tech. Acc. #3: Prelim. Cell Testing

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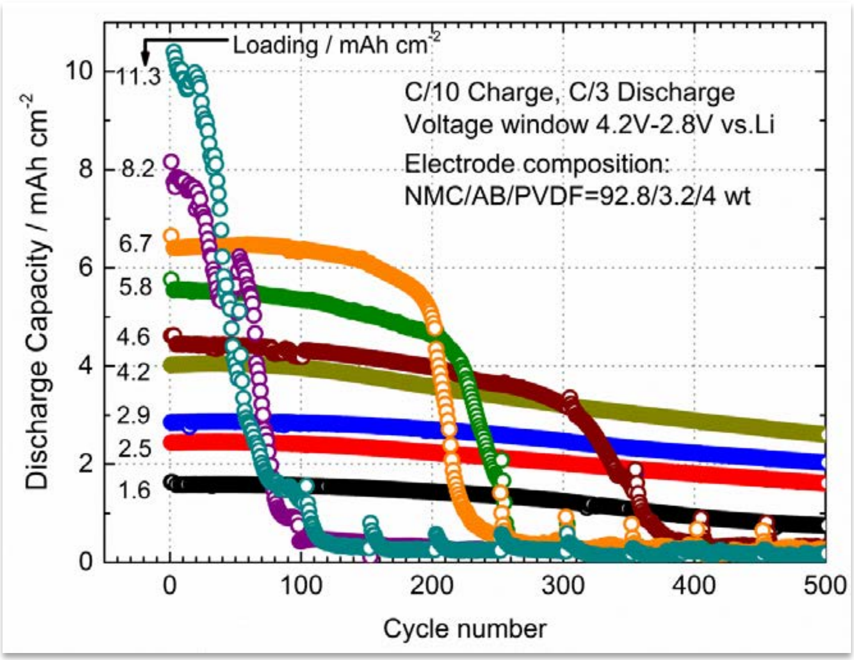
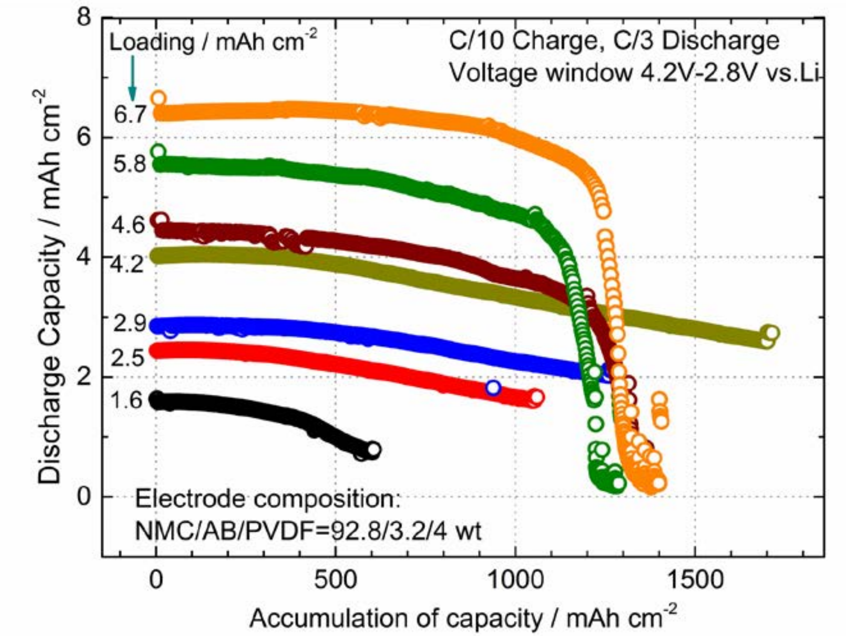
Laminate Thickness on Cycle Life

Cycle Number



Throughput



Is this the lithium or something else?

Collaboration and Coordination

Partnerships / Collaborations	
ARKEMA INNOVATIVE CHEMISTRY	Provides binders of PVdF of different molecular weights, some blends, and some experimental binders.
umicore	Provided baseline active material.
BLACK DIAMOND STRUCTURES	Provides a conductive carbon additive that enhances the cohesive strength of the laminate.
DAIKIN	Provides battery-grade electrolyte.
BYU	Provides separators and performs calculations of the drying configurations of particles in electrodes.
Hydro Québec	Provides current collectors, other cell parts, equipment for making cells, and expertise on cell manufacturing.
APPLIED SPECTRA	Provides measurement of electrode composition as a function of depth from the surface.
BERKELEY LAB	Colleagues provide capabilities in macroscopic modeling and characterization of laminates using the techniques at the ALS and NCEM.

Remaining Challenges and Barriers

- When moving to higher viscosity slurries, what is the impact on mixing time and energy input?
- What is the impact of drying time?

- We've seen cycling to higher voltages result in secondary particle fracture, we would prefer to avoid promoting this through calendering.
- Can we develop a less intusive cross-sectioning technique?
- How many cycles do calendered cells take to recover their thickness?
- Can binder amount or MW mitigate this?
- Is this a result of electrode memory or the production of solid material from side reactions?
- What happens to the other cell components?

- To what extent is the optimum binder content a function of molecular weight?
- Is there an ideal molecular weight of the binder?
- We should be able to characterize the yield stress of the electrodes subjected to bend tests through established continuum mechanics calculations.

- What are the real-world manufacturing limitations to fabricating high loading electrodes?
- What is the impact of drying speed on these results.
- Can the drying time remain at the industry level of *ca*. 3 min. with recommended changes in polymer and slurry viscosity?

Proposed Future Work

Summary of Research

- Calendering:
  - We've recorded no mechanical advantages to calendering at higher temperatures
  - Monotonically improves power capability down to a porosity of 30%.
  - Flattens particles on the surface
  - Weakens the cohesion of the secondary particles throughout the laminate.
  - Resists expansion in electrolyte for at least a week.
  - Effects fade with cycling.
- Mechanical Strength (bend test):
  - The laminates showed fractures before delaminating.
  - There appears to be an optimum level of binder (~3%) for thick electrodes under hoop stress.
  - Calendering allows for smaller radius wrappings before fracturing.
  - Treated carbon nanotubes can be uniformly dispersed in a laminate.
  - A small amount of carbon nanotubes (`0.2%) appears to provide significant resistance to fracture.
- Cycling Performance:
  - Electrodes of very high loading can still deliver most of the energy and provide the necessary 30-sec pulse power at 80% DOD.
  - Electrodes of extremely high loading are capable of delivering most of the cells energy at C/3 and can deliver the necessary pulse power.
  - Preliminary result s show thinner electrodes can have a higher throughput of energy than thicker electrodes
- Carbon/binder interface
  - Preliminary results indicate that a carbon/binder layer on the current collector improves adhesion.(not shown).

Key Challenges

- Is their any amount of calendering that does not weaken the secondary particles?
- Understanding the cycle life of thick electrodes *versus* standard thickness electrodes.
- Can we produce cells with a reference electrode that cycle as long as cells without a reference electrode?
- Understanding the manufacturing limitations of making very high loading electrodes (casting , drying).

Proposed Follow-on Work

<u>Research</u>

- Establish a correlation between yield stress and binder content
- Determine the minimum porosity without particle fracture.
- Develop a less intrusive electrode cross-sectioning technique.
- Establish a set-up for reducing drying times to 3 min.
- Investigate impact of electrode viscosity on mixing time and energy input.
- Produce cells with a reference electrode to eliminate impedance rise effects of the anode on cycling behavior.

<u>Fabrication</u>

- Establish general correlations between material attributes and electrode processibility.
- Meet with competent electrode manufacturers and understand the limitations of proposed changes to processing conditions.
- Consider compromises in materials and processing conditions that could be implemented on today's fabrications lines to increase electrode loadings without impacting cost.

Any proposed future work is subject to change based on funding levels.

Summary

- **Relevance**
  - The work is focused on increasing the energy density of electrodes, a top VTO priority; this, in turn, will reduce system cost, another top priority.
- **Approach**
  - Assess affect of material properties on processing conditions, and electrode uniformity and quality, by testing different active material sizes, binders, and conductive agents.
  - Assess change of processing conditions on electrode quality and performance (power, energy, and life.)
  - Use advanced diagnostics to provide understanding between materials, processing, and electrode quality.
- **Major Technical Accomplishments**
  - Begun scoping of material effects on electrode uniformity; assessed effects of:
    - Binder source
    - Binder molecular weight
    - Addition of NMP (viscosity)
    - Height of doctor blade
    - Casting speed
  - Used EDX to measure electrode atomic composition from current collector to surface.
- **Future Work**
  - Measure and establish correlations of materials properties to slurry properties to electrode mechanical properties to electrode performance.
  - Assess additional processing conditions
    - Mixing time
    - Drying rate

Any proposed future work is subject to change based on funding levels.